

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
4 March 2004 (04.03.2004)

PCT

(10) International Publication Number
WO 2004/018764 A1

- (51) International Patent Classification⁷: **D06L 1/00**
- (21) International Application Number:
PCT/GB2002/003828
- (22) International Filing Date: 20 August 2002 (20.08.2002)
- (25) Filing Language: English
- (26) Publication Language: English
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- (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Published:
— with international search report
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- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: METHOD FOR CONDITIONING TEXTILES

(57) Abstract: Fatty branched polyalkoxylates, particularly of the formula: $R^1O(AO)_mR^2$ (I) where R^1 is C_8 to C_{30} aliphatic hydrocarbyl or acyl; AO is predominantly branched alkyleneoxy, particularly propyleneoxy; m is from 2 to 50; and R^2 is H or a is C_1 to C_4 aliphatic hydrocarbyl or acyl, are used as fabric conditioners in CO_2 based dry cleaning systems. The cleaning medium may include detergent surfactant and/or non surfactant cleaning additive or may be free from such additives in which case the treatment can be provided in a rinse cycle in a cleaning process.

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Conditioning Textiles

This invention relates to conditioning textile materials and products including clothes, particularly as part of a dry cleaning process, using liquid carbon dioxide (CO₂) and conditioning agents, particularly branched polyalkyloxylate conditioning agents for the textiles.

- 5 The dry cleaning of clothes using fluid carbon dioxide, either as liquid or supercritical fluid, is known from many patents. An early suggestion is in US 4012194 (Maffei) which teaches simply using liquid carbon dioxide as a substitute for halocarbon solvents e.g. perchlorethylene (perc), used in conventional dry cleaning. Later patents develop approaches using detergent materials, including US Patents US 5676705, US 5683473, US 5683977, US 6131421, US 6148644, and US 6299652
10 assigned to Unilever and their equivalents, which relate to the use of defined detergents based on various classes of polymers and a series of cases, including US Patents 5858022, 6200352, 6280481, 6297206, 6269507 and US published application 200106053 A, assigned to MiCell and their equivalents. Also US 5279615 assigned to Chlorox Co uses cleaning non-polar organic cleaning adjuncts, especially alkanes, in densified, particularly supercritical CO₂.
- 15 The major emphasis in these documents is to enhance the cleaning performance of the CO₂. However, other attributes of the cleaning system are also important in practice, in particular the ease of handling of textiles particularly clothes after cleaning, the ease with which subsequent steps, such as ironing, can be carried out and the appearance and feel of clothes in the hands of the end customer.
- 20 This invention is based on our finding that the inclusion of fatty branched polyalkoxylates, particularly fatty alcohol, branched polyalkoxylates, especially propoxylates, in CO₂ cleaning systems gives improved softness and handling characteristics to textiles, particularly clothes, after treatment.

The invention accordingly provides a method of dry cleaning which includes a conditioning step in
25 which textile material, particularly clothes, is contacted with a treatment medium based on liquid CO₂ and which includes from 0.001 to 2.5% by weight of the treatment medium of a conditioning agent which includes at least one fatty alcohol or fatty acid branched polyalkyloxylate.

- The term "branched polyalkyloxylate" refers to polyalkoxylate chains including a substantial proportion of units which have side chains e.g. as provided by propyleneoxy or butyleneoxy units.
- 30 The term "fatty branched polyalkyloxylate" refers collectively to branched polyalkyloxylate based on fatty alcohols or fatty acids. In describing the medium as "based on liquid CO₂" we mean that the medium is liquid CO₂ which may include additives, in addition to the conditioning agent.

Desirably the alcohol branched polyalkyloxylate is of the formula (I):



35 where

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R¹ is a C₈ to C₃₀ aliphatic hydrocarbyl group, particularly an alkyl or alkenyl group, or a C₈ to C₃₀ aliphatic acyl group;

AO is an alkyleneoxy group and is at least predominantly branched alkyleneoxy, particularly propyleneoxy;

5 m is from 2 to 50, particularly 2 to 30; and

R² is H or a is a C₁ to C₄ aliphatic hydrocarbyl group, particularly an alkyl group, or a C₁ to C₄ acyl group, particularly an acetyl group.

When the group R¹ is an aliphatic hydrocarbyl group, particularly an alkyl or alkenyl group. Within the chain length range C₈ to C₃₀, the group has from C₈ to C₂₂, particularly C₁₂ to C₂₀, and
10 especially C₁₆ or C₁₈, carbon atoms. The hydrocarbyl group is desirably an open chain group and may be linear or branched or a mixture of linear and branched chains. The groups may be saturated or unsaturated or a mixture of saturated and unsaturated groups.

When the group R¹ is an aliphatic acyl group, desirably it has from C₈ to C₂₂, particularly C₁₂ to C₂₀, and especially C₁₆ or C₁₈, carbon atoms. The acyl group is desirably an open chain group
15 and may be linear or branched or have a mixture of linear and branched chains. The chains may be saturated or unsaturated or a mixture of saturated and unsaturated chains.

The alkyleneoxy groups, -AO-, are typically all C₂ to C₄ groups while being predominantly branched alkyleneoxy e.g. propyleneoxy and/or butyleneoxy. In this context "predominantly" means that the molar proportion of branched alkyleneoxy residues in the polyalkyleneoxy chain is at
20 least 50%. Desirably all the residues are all propyleneoxy and/or butyleneoxy residues. Mixed alkylene oxide chains may be used such as:

mixtures of propyleneoxy and butyleneoxy residues, when the molar ratio of propyleneoxy residues to butyleneoxy residues will usually be from 99:1 to 1:99 (more extreme ratios substantially correspond to chains made entirely of the majority residue), more usually from 10:1 to 1:10;

25 mixtures of propyleneoxy and ethyleneoxy residues, when the proportion of ethyleneoxy residues will usually not be more than 20%, more usually not more than 10% and desirably not more than 5%, of the total of propyleneoxy and ethyleneoxy residues; or

mixtures of butyleneoxy and ethyleneoxy residues, when the proportion of ethyleneoxy residues will usually not be more than 50%, more usually not more than 25% and may be not more than
30 10%, of the total of butyleneoxy and ethyleneoxy residues.

When the alkyleneoxy residues are mixed, the polyalkyleneoxy chain can be a random or block copolymeric chain. Within the range 2 to 50), m is desirably 2 to 30, more usually 5 to 25 and usually 7 to 20. The number of units in the polyalkyleneoxy chain, 'm', is an average value and may be non-integral.

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The group R^2 is H, or an end capping group such as a lower alkyl group e.g. a C_1 to C_4 alkyl group, and when other than H is desirably a methyl or ethyl group, or a C_1 to C_4 acyl group, particularly an acetyl group.

5 It is further desirable that the combined number of carbon atoms in the groups R^1 and R^2 is from 9 to 26 particularly from 15 to 24.

Desirably in compounds of the formula (I) used in this invention, the ratio of carbon atoms in the groups R^1 to the number of repeat units in the polyalkylene oxide chain $-(AO)_n-$ is from 8:1 to 1:4, particularly 6:1 to 1:2.

10 The amount of the conditioning agent alcohol branched polyalkyloxylate present in the cleaning medium is from 0.001 to 2.5%, usually from 0.005 to 2%, more usually from 0.01 to 1%, particularly from 0.01 to 0.1% and more particularly from 0.01 to 0.5% by weight of the cleaning medium. The use of lower amounts of conditioning agent will not generally give useful results and use of larger amounts does not appear to give additional benefits and may result in including so much conditioning agent in the system that conditioning agent residues are deposited onto the textiles
15 being cleaned or left on the walls of the cleaning apparatus.

Cleaning additive materials i.e. materials that improve the cleaning performance of liquid CO_2 , can be included in the cleaning system. Typically such cleaning additives can be viewed as either detergent surfactants or non-surfactant cleaning additives.

20 The invention accordingly includes a method of dry cleaning which includes contacting textile material, particularly clothes, with a dry cleaning treatment medium based on liquid CO_2 and including from 0.001 to 2.5% by weight of the treatment medium of a conditioning agent which includes at least one fatty, particularly fatty alcohol, branched polyalkyloxylate, desirably of the formula (I) as defined above, in combination with at least one detergent surfactant and/or non-surfactant cleaning additive.

25 Detergent surfactants are materials that modify the interfacial properties of soils so that they are more readily separated from the textiles, particularly clothes on which the soil initially lies, and/or that the surfactant acts to minimise or prevent the re-deposition of soil onto the textiles. In aqueous systems, the structures of typical detergent surfactant compounds are well known, but in liquid CO_2 the nature of materials having useful detergent surfactant properties can be very
30 dissimilar to those useful in aqueous systems. A wide range of detergent surfactants can be used in the present invention and examples of suitable types of detergent surfactants are given in the specifications referred to above.

Non-surfactant cleaning additives are materials, usually liquids which are miscible with liquid CO_2 or are solids which are soluble in liquid CO_2 , which enhance the cleaning performance of CO_2 but
35 are not surfactants. It is thought that such materials function to dissolve or soften soils that would

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otherwise not be removed well by liquid CO₂ or combine with the liquid CO₂ to enhance its solvent or soil softening properties. At least some such materials have been viewed as co-solvents in combinations with liquid CO₂.

Among such non-surfactant cleaning additives are relatively polar multi-esters i.e. compounds which have 2 or more carboxylic acid ester groups and generally a molecular weight of not more than 750, particularly of the formula (II):



where

X is -C(O)O- or -OC(O)-; such that

10 where X is -C(O)O-,

R¹¹ is a direct bond or the residue of a C₁ to C₁₀ hydrocarbyl group from which n hydrogen atoms have been removed; and

R¹² is a C₁ to C₁₀ hydrocarbyl group; and

where X is -OC(O)-,

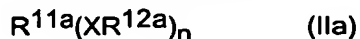
15 R¹¹ is or the residue of a C₂ to C₁₀ hydrocarbyl group from which n hydrogen atoms have been removed; and

R¹² is H or a C₁ to C₁₀ hydrocarbyl group; and

n is from 2 to 5;

the compound having a molecular weight of not more than 750.

20 Such cleaning additive multi-esters can be divided into two sub-classes respectively of the formulae (IIa) and (IIb) below. Compounds of the formula (IIa) are esters of a multi-carboxylic acid and a mono-hydroxy alcohol:



where

25 X is -C(O)O-;

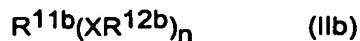
R^{11a} is a direct bond or the residue of a C₁ to C₁₀ hydrocarbyl group from which n hydrogen atoms have been removed;

R^{12a} is a C₁ to C₁₀ hydrocarbyl group; and

the compound having a molecular weight of not more than 750.

30 Examples of compounds of the formula (IIa) include di-esters of dicarboxylic acids such as succinic, glutaric and adipic acids.

Compounds of the formula (IIb) are esters of a monocarboxylic acid and a multi-hydroxy alcohol:



where

35 X is -OC(O)-;

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R^{11b} is or the residue of a C₂ to C₁₀ hydrocarbonyl group from which n hydrogen atoms have been removed; and

R^{12b} is H or a C₁ to C₁₀ hydrocarbonyl group; and

the compound having a molecular weight of not more than 750.

- 5 Examples of compounds of the formula (IIb) include esters of multi-hydroxyl compounds such as triacetin (glycerol triacetate), ethylene glycol diacetate and pentaerythritol tetra-acetate.

- The invention accordingly includes a method of dry cleaning which includes contacting textile material, particularly clothes, with a dry cleaning treatment medium based on liquid CO₂ and including from 0.01 to 5% by weight of the treatment medium of a conditioning agent which
- 10 includes at least one fatty branched polyalkyloxylate, desirably of the formula (I) as defined above, in combination with a cleaning additive, desirably at from 0.01 to 5% by weight of the cleaning medium, which is at least one multi-ester desirably having a molecular weight of not more than 750.

- The invention further includes a, desirably detergent surfactant free, dry cleaning medium based on liquid CO₂ and including:
- 15

- a from 0.01 to 5% by weight of the cleaning medium of a cleaning additive which is at least one multi-ester having a molecular weight of not more than 750, and desirably of the formula (II) as defined above; and
- b from 0.01 to 5% by weight of the treatment medium of a conditioning agent which includes at
- 20 least one fatty branched polyalkyloxylate, desirably of the formula (I) as defined above.

Desirably the multi-ester used in this aspect of the invention, both method and composition, is a compound of the formula (II), especially (IIa), above, and particularly a dimethyl ester of adipic, glutaric or succinic acids or a mixture of such esters.

- Within the formula (II) above, generally is desirable that the group X is -C(O)O- as these
- 25 compounds seem to provide superior effects in cleaning. Among such compounds, the group R¹¹ is desirably -(CH₂)_p- where p = 2 to 6, particularly 2 to 4 and especially as in the mixed ester of succinic, glutaric and adipic acids; and the group R¹² is desirably methyl, ethyl or propyl, particularly methyl. Thus, the dimethyl esters of succinic, glutaric and adipic acids, particularly as mixtures are particularly desirable additives.

- 30 The molecular weight of the cleaning additive is desirably not more than 750 and is desirably not more than 500. In practice the molecular weight for individual components e.g. of formula (I) can be as low as 118 (dimethyl oxalate) but will not usually be lower than 146 (dimethyl succinate and ethylene glycol diacetate). More usually on average the molecular weight will be at least 150, particularly from 150 to 300. The mixed dimethyl esters of succinic, glutaric and adipic acids can
- 35 have molecular weights ranging from about 150 to 170 e.g. for an approximately 1:1:3 mixture the average molecular weight is about 165.

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In order to maintain the desired high polarity, the ratio of oxygen to carbon atoms in the molecules of the cleaning additive is (on average) desirably from 1:1 to 1:5 particularly from 1:1 to 1:3 and especially from 1:1 to 1:1.5. The mixed dimethyl esters mentioned above have an average ratio of ca 1:1.23.

- 5 The amount of cleaning additive multi-ester used will typically be from 0.01 to 5%, usually from 0.05 to 2%, more usually from 0.1 to 1%, particularly from 0.1 to 0.5% and more particularly from 0.1 to 0.3% by weight of the cleaning medium. The use of lower amounts of cleaning additive will not generally give useful results and use of larger amounts does not appear to give additional benefits and may result in including so much additive in the system that additive residues are
10 deposited onto the textiles being cleaned or left on the walls of the cleaning apparatus.

When fatty alcohol branched polyalkyloxyate conditioning agents are used in combination with such multi-ester cleaning agents the amount of fatty branched alkoxyate will typically be from about 2 to about 20%, desirably from about 5 to about 15% and particularly about 10% of the total additive combination.

- 15 Other ingredients can be included in the dry cleaning formulation such as fragrances, optical brighteners, sizes e.g. starch, enzymes, bleaches, particularly peroxide bleaches e.g. organic and/or inorganic peroxides or hydrogen peroxide or a source of hydrogen peroxide.

- The textiles to be cleaned will usually be garments and can be of woven or non-woven fabrics. The fibre making up the fabric can be or include a wide range of natural and synthetic fibres including
20 polyamides particularly natural polyamides such as silk and wool and synthetic polyamides such as nylon, cellulosic fibres such as cotton, linen and rayon, synthetic polymers such as polyester, particularly polyethylene terephthalate or related copolymers, or acetate polymers. When fabrics including acetate polymers and possibly nylon polymers are cleaned it is best to avoid direct contact between the fabric and high concentrations of or neat multi-ester additives. When neat or
25 at high concentration, the multi-ester additives may swell or dissolve such polymers leading to fabric damage. Thus it is desirable to pre-mix the multi-ester with CO₂ before permitting contact with such polymers. Pre-mixing the multi-ester cleaning additive with CO₂ to give a concentration of less than about 10%, more usually less than 5%, and desirably not more than 2% by weight of the cleaning additive in the liquid CO₂ based cleaning medium before the additive comes into
30 contact with the textile seems to avoid this potential problem.

- The particular mode of operation will depend on the equipment used. Generally the cleaning will be carried out in a drum, which may have its axis vertical or horizontal. The textiles are introduced into the drum which is then sealed and filled with the cleaning medium including carbon dioxide typically to give a mixture of liquid and gaseous CO₂ in the drum. The textiles and liquid CO₂
35 based cleaning medium are then agitated to give thorough mixing and contact between the

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cleaning medium and textiles. The textiles will be contacted with the cleaning medium for a time adequate to clean the textiles to the desired extent. The cleaning medium is then separated from the textiles, typically by draining or venting it from the drum. Generally the textiles will be subject to one such cleaning cycle, but if desired the cleaning cycle may be repeated to obtain a higher degree of cleaning. Usually, the textiles are subject to at least one rinse cycle with liquid carbon dioxide usually not including cleaning additives, but which may include fabric softeners, optical bleaches etc if desired. The rinse liquid is similarly separated from the textiles, which can then be recovered by de-pressurising the drum and opening it to remove the textiles. One potentially advantageous way of carrying out this invention is to include the conditioning agent in the rinse cycle. This may mitigate the disadvantage noted above that combining the conditioning agent in the cleaning cycle with a cleaning agent may have detrimental effects on the cleaning performance. Though this can be managed, as is described above, the problem can be side stepped by including the conditioning agent in a rinse cycle.

The invention accordingly includes method of dry cleaning which includes contacting textile material, particularly clothes, with a dry cleaning treatment medium based on liquid CO₂ and including from 0.001 to 2% by weight of the treatment medium of a conditioning agent which includes at least one fatty branched polyalkyloxylate, the treatment medium not including any cleaning additives. Desirably in this aspect of the invention the treatment stage is applied as a rinse stage following a previous cleaning stage, which can be by liquid CO₂, desirably including at least one detergent and/or non-detergent cleaning additive.

In particular, in this aspect, the invention provides a method of dry cleaning which includes the steps of :

- a contacting textile material with a dry cleaning medium based on liquid CO₂ and which is desirably detergent surfactant free, and which includes from 0.01 to 5% by weight of the cleaning medium of a cleaning additive which is at least one multi-ester, desirably of the formula (II), particularly (IIa), defined above, having a molecular weight of not more than 750;
- b separating the textiles and the dry cleaning medium; and subsequently
- c contacting the textile material with a treatment medium based on liquid CO₂ and including from 0.001 to 2.5% by weight of the treatment medium of a conditioning agent which includes at least one fatty branched polyalkyloxylate, desirably of the general formula (I) as defined above; and desirably
- d separating the textiles and the treatment medium.

Any suitable apparatus for dry cleaning with liquid carbon dioxide can be used. Typically such apparatus includes a drum in which the cleaning is carried out. The drum may have its axis horizontal or vertical. (Other angles of orientation will generally be less convenient in operation.) Providing agitation in a horizontal axis drum can simply be by rotation around its axis. Vertical axis

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drums will usually include an agitator which can be moved to agitate the drum contents. Other means of agitation include paddles or vanes in the drum or by jetting liquid CO₂ into the mixture of cleaning medium and textiles in the drum. Suitably vigorous agitation may give rise to cavitation in the cleaning medium and this may improve the cleaning performance.

- 5 Typically the cleaning temperature will be from -10 to 25°C, more usually from 5 to 25°C, particularly from 10 to 20°C. The operating temperature will not usually be above about 25°C to maintain the cleaning medium a reasonable margin from the critical point of CO₂, as supercritical CO₂ may extract textile dyes from fabrics. Operating at or near ambient temperature simplifies operation of the process, but using a lower temperature means that the CO₂ is more dense and a
- 10 more effective cleaning agent. Temperatures in the range 10 to 17°C, particularly 12 to 15°C generally provide a reasonable balance of properties and are thus advantageous.

During cleaning the cleaning medium must be kept at a pressure which maintains the CO₂ at least partially as a liquid. This will usually be the vapour pressure of the cleaning medium at the temperature of operation because, as is noted above, it is desirable for both liquid and gaseous

- 15 CO₂ to be present. At the typical operating temperatures noted above, the corresponding pressures are approximately 2.7 to 6.4 MPa, more usually from 4 to 6.4 MPa, particularly from 4.5 to 5.7 MPa and balancing density and temperature 4.5 to 5.5 MPa, particularly from 4.9 to 5.1 MPa.

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The invention is illustrated by the following Examples. All parts and percentages are by weight unless otherwise indicated.

Materials

FCA1 C18 linear alcohol 5-propoxylate

5 FCA2 C24 guerbet alcohol 5-propoxylate

FCA3 C24 guerbet 11-propoxylate

FCA4 C24 guerbet 24-propoxylate

FCA5 C18 linear alcohol 11-propoxylate

10 ME1 mixed esters: dimethyl adipate (ca 60%), dimethyl glutamate (ca 20%), and dimethyl succinate (ca 20%)

CD2 Fabritech 5565 - conventional formulated detergent surfactant

CD3 Conventional detergent surfactant (composition not known)

Cleaning testing used standard "Krefeld" stained cloths. The codes for these cloths include a number indicating the fabric type and a letter or letters indicating the soil as follows:

Cloth Type		Soil Type			
10	cotton	C	WFK soil*/lanolin mix	GM	used motor oil
20	polycotton	D	sebum	TE	clay
30	polyester (PET)	LS	Lipstick	PF	pigment/vegetable fat

15 * WFK soil - a mixed soil based on kaolinite and containing soot and iron oxide pigments

Cleaning effectiveness - was assessed spectrometrically (using an X-Rite Spectrophotometric Colour Measurement system) by comparison of commercially available standard soiled cloths before and after cleaning with the results given as % stain removal.

Example 1

20 A number of fabric conditioning fluids were made up based on liquid CO₂ and were used to treat textile samples. The compositions are set out in Table 1 below:

Table 1

Ex No	Additive		Run No
	type	amount	
1.1	FCA1	0.1	1.1.1
		0.2	1.1.2
1.2	FCA1	0.1	1.2.1
1.3	FCA1	0.1	1.3.1
1.4	FCA1	0.1	1.4.1
1.5	FCA1	0.2	1.5.1

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Example 2

Further tests were carried out in commercial scale liquid CO₂ dry cleaning equipment using standard Krefeld soiled cloths, pinned to blank textile sheets to provide more realistic behaviour in the cleaning machine. The results are set out in Table 2 below:

5

Table 2

Ex No	Cleaning Additive		Conditioner		30C	30D	20MU	10LS	10PF	10TE	10GM
	type	%	type	%							
2.1.c1	-	0	-	0	37.6	63.6	31.7	37.9	40.5	17.8	25.9
2.1.c2	CD3	0.2	n/a	-	45.1	63.4	32.9	35.6	39.8	21.9	23.1
2.1	ME1	0.18	FCA1	0.02	35.7	63.5	21.5	34.5	45.3	31.7	20.6
2.2.c1	-	0	-	0	41.6	55.1	30.7	36.2	37.6	17.8	26.1
2.2.c2	CD2	0.2	n/a	-	20	35.3	21.4	32.1	29	14	21.6
2.2	ME1	0.18	FCA1	0.02	47.7	59.9	36.3	37.9	45.9	28.4	29.5

The textiles cleaned using combined cleaning and conditioning additives according to the invention had much improved feel on removal from the cleaning machines and were less wrinkled and easier to iron than those cleaned with liquid CO₂ alone or using the commercial detergent surfactant additives.

10

Claims

- 1 A method of dry cleaning which includes a conditioning step in which textile material is contacted with a treatment medium based on liquid CO₂ and which includes from 0.001 to 2.5% by weight of the treatment medium of a conditioning agent which includes at least one fatty alcohol or fatty acid branched polyalkyloxylate.
- 5 2 A method as claimed in claim 1 wherein the alcohol branched polyalkyloxylate is of the formula (I):
- $$R^1O(AO)_mR^2 \quad (I)$$
- where
- 10 R¹ is a C₈ to C₃₀ aliphatic hydrocarbyl or acyl group;
 AO is an alkyleneoxy group and is at least predominantly branched alkyleneoxy;
 m is from 2 to 30; and
 R² is H or a is a C₁ to C₄ aliphatic hydrocarbyl or acyl group.
- 3 A method as claimed in claim 2 wherein the group R¹ is a C₈ to C₂₂ alkyl or alkenyl group.
- 15 4 A method as claimed in claim 2 wherein the groups AO are propyleneoxy and/or butyleneoxy groups.
- 5 A method as claimed in claim 2 wherein the group R² is H, a methyl or ethyl group, or an acetyl group.
- 6 A method as claimed in claim 2 wherein m is from 2 to 30.
- 20 7 A method as claimed in any one of claims 1 to 6 wherein the concentration of the conditioning agent alcohol branched polyalkyloxylate in the cleaning medium is 0.01 to 1% by weight of the cleaning medium.
- 8 A method as claimed in any one of claims 1 to 7 wherein the textile material is contacted with a dry cleaning treatment medium further including at least one detergent surfactant and/or non-surfactant cleaning additive.
- 25 9 A method as claimed in claim 8 wherein the non-surfactant cleaning additive is a multi-esters of the formula (II):
- $$R^{11}(XR^{12})_n \quad (II)$$
- where
- 30 X is -C(O)O- or -OC(O)-; such that
 where X is -C(O)O-,
 R¹¹ is a direct bond or the residue of a C₁ to C₁₀ hydrocarbyl group from which n hydrogen atoms have been removed; and
 R¹² is a C₁ to C₁₀ hydrocarbyl group; and
 35 where X is -OC(O)-,

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R¹¹ is or the residue of a C₂ to C₁₀ hydrocarbyl group from which n hydrogen atoms have been removed; and

R¹² is H or a C₁ to C₁₀ hydrocarbyl group; and

n is from 2 to 5;

5 the compound having a molecular weight of not more than 750.

10 A method as claimed in any one of claims 1 to 7 wherein the textiles are contacted with the conditioning treatment medium, which does not include any cleaning additives, in a rinse cycle.

11 A dry cleaning medium based on liquid CO₂ and including:

10 a from 0.01 to 5% by weight of the cleaning medium of a cleaning additive which is at least one multi-ester having a molecular weight of not more than 750; and

b from 0.01 to 5% by weight of the treatment medium of a conditioning agent which includes at least one fatty branched polyalkyloxylate,

12 A dry cleaning medium as claimed in claim 11 which is free of detergent surfactant.

15 13 A dry cleaning medium as claimed in either claim 11 or claim 12 wherein the fatty branched polyalkyloxylate is of the formula (I) as defined in any one of claims 2 to 6.

14 A dry cleaning medium as claimed in any one of claims 11 to 13 wherein the multi-ester is of the formula (II) as defined in claim 9.

20 15 A dry cleaning medium as claimed in any one of claims 11 to 14 which additionally includes at least one of fragrances, optical brighteners, sizes, enzymes and/or bleaches.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 02/03828

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 D06L1/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 D06L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 858 022 A (CAUBLE DAVID F ET AL) 12 January 1999 (1999-01-12) cited in the application	1-8
A	column 2, line 32 - line 42 column 3, line 14 - line 18 ---	9-15
X	US 6 200 352 B1 (CAUBLE DAVID F ET AL) 13 March 2001 (2001-03-13) cited in the application	1-8
A	column 3, line 57 - line 61 column 4, line 3 column 4, line 16 - line 28; claims --- -/--	9-15

☒ Further documents are listed in the continuation of box C.

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Date of the actual completion of the international search

27 May 2003

Date of mailing of the international search report

13/06/2003

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 02/03828

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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A	<p>US 2002/010965 A1 (RACETTE TIMOTHY L ET AL) 31 January 2002 (2002-01-31) page 6, paragraph 154 - paragraph 161 page 5, paragraph 73 -page 6, paragraph 153 page 10, paragraph 236; claims; tables 1,2 -----</p>	1-15

INTERNATIONAL SEARCH REPORT

information on patent family members

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